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**A PRELIMINARY REVIEW OF ORGANIC MATERIALS
SINGLE CRYSTAL GROWTH BY THE CZOCHRALSKI
TECHNIQUE**

By B. G. Penn, A. W. Shields, and D. O. Frazier

Space Science Laboratory
Science and Engineering Directorate

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TECHNICAL MEMORANDUM

A PRELIMINARY REVIEW OF ORGANIC MATERIALS SINGLE CRYSTAL GROWTH BY THE CZOCHRALSKI TECHNIQUE

I. INTRODUCTION

The purpose of this paper is to review the experimental methods presented in several key papers to grow organic single crystals by the Czochralski (CZ) method to help establish a basis for the growth of high quality single crystals of organic materials for nonlinear optical devices. Another goal is to examine the feasibility of growing organic single crystals in microgravity.

The development of organic materials for use in nonlinear optical devices is of interest because their nonlinearities may be orders of magnitude larger than conventional inorganic materials such as lithium niobate and potassium dihydrogen phosphate [1-7]. Moreover, organic materials offer flexibility of molecular design, promise of virtually an unlimited number of crystalline structures, purification by conventional methods, and a high damage resistance to optical radiation. Consequently, these materials might make it possible to replace electronic switching circuits in computing and telecommunication systems by purely optical devices. In optical information processing, this may offer the potential for extremely high throughput, compact information processing systems.

The growth of high quality crystals is required for the use of organic materials in nonlinear optical devices. One reason for this is that inhomogeneities in optical materials give rise to variations in the refractive index or absorption which results in distortion of the optical beam to be processed [8]. In optical devices these distortions give rise to a high signal-to-noise ratio in a device. As a rule, the problem of inhomogeneities becomes more serious as the nonlinearities of materials become larger. Traditionally, crystals of organic materials have been grown from the melt by the Bridgman technique [9]; however, this technique suffers from mechanical damage introduced by the container wall. This can be especially detrimental for many organic materials that have very poor mechanical properties. The CZ method offers the advantage that it is essentially container free with respect to the growing crystal. Further improvement in the quality of organic single crystals grown by the Czochralski method might be accomplished by performing crystal growth in microgravity where gravity driven convection is eliminated.

II. REVIEW OF SOME KEY WORK ON GROWTH OF SINGLE CRYSTALS OF ORGANIC COMPOUNDS BY THE CZOCHRALSKI METHOD

The advantage of the Czochralski method for the growth of single crystals of organic compounds in comparison to growth by the Bridgman or vapor methods is that it is essentially container free with respect to the growing crystal. This is very important for the growth of high-quality single crystals of organic compounds that have poor mechanical properties. To be a candidate for use in growth of single crystals by the Czochralski method, organic compounds should have comparatively low melting points with respect to their molecular weight [10]. This is desirable because sublimation problems are reduced with these compounds since the

sublimation vapor pressure decreases exponentially with decreasing temperature. In addition, the material should not decompose before melting.

Single crystals of benzil, whose nonlinear optical properties have been measured, have been grown by the Czochralski method [11]. This compound crystallizes in the helical state and the crystal is noncentrosymmetric. The d_{11} value was found to be $(11.2 \pm 1.5) \times d_{11}$ of α quartz [12]. The apparatus used by Bleay et al. [11] to grow single crystals of benzil is shown in Figure 1. The melt was contained in Pyrex glass crucible (A) surrounded by an aluminum pot (B) to obtain an even temperature distribution and high thermal inertia. A Pyrex pipe section (C), bolted and sealed to the furnace, provided an enclosure for the growing crystal and permitted the control of the surrounding atmosphere by ports (D). Undesirable condensation on the glass was prevented by heaters wound on (C). The pulled crystal was similarly protected by heater (E). The concentric water-cooled pipe (F), which had a small seed crystal attached at one end, was slowly withdrawn by means of a motor-driven lead screw. The growth rates were typically in the range 0.1 to 0.5 mm h^{-1} . Growth was initiated by lowering a Bridgman or solution-grown seed crystal, attached to seed holder, into the melt and reducing the temperature until growth occurred. The apparatus was left to equilibrate for several hours before pulling was commenced. The analysis of perfection by X-ray topography indicated that the crystals, which had dimensions up to 10 cm³, contained substantial volumes which were essentially dislocation free. The Czochralski grown crystals had substantially less dislocations than generally contained in Bridgman crystals. Katoh and Kato [13] grew more perfect crystals of benzil by repeated Czochralski growth. In this method, the defect containing part of a crystal, grown by the Czochralski method, was etched off and the rest used as a seed for further growth. With this method dislocation-free crystals having a cross section of

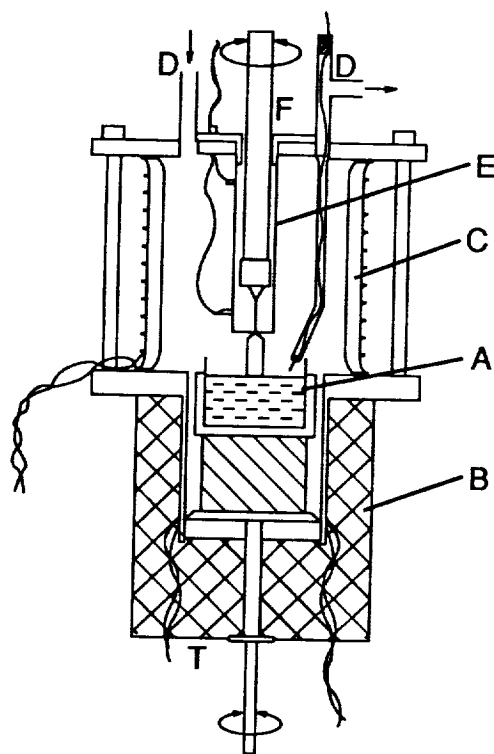


Figure 1. Czochralski apparatus used by Bleay et al. [11] to grow single crystals of benzil.

several mm square and more than 10 mm in length were grown. The properties and processing parameters of benzil and other organic compounds used to grow single crystals by the Czochralski method are summarized in Table 1.

Other organic compounds used to grow single crystals by the Czochralski method are benzophenone, 12-tricosanone (laurone), and salol. Benzophenone single crystals were grown by Bleay et al. [11] using the procedure and apparatus (Fig. 1) described for benzil in the previous paragraph. The crystals, which had dimensions up to 10 cm³, had fewer dislocations than commonly obtained by the Bridgman technique. Cook and Gwan [14] grew large single crystals of laurone using the apparatus shown in Figure 2. The laurone was placed in a crucible and outgassed by melting and freezing under high vacuum. Purified argon was admitted to 50 kPa to suppress evaporation. The seed crystals were grown using a stainless steel rod with holes drilled as shown in Figure 2 by freezing a small amount of laurone onto it. The rod was raised until it was just in contact with the melt and pulling was started at 1 cm/day. The resulting boule was necked three times in an effort to grow a suitable seed crystal. Finally, a crystal 4 mm x 5 mm x 15 mm was obtained by this process. Inoue et al. [15] grew salol crystals by the Czochralski method and examined dislocations using the etch pit method and X-ray topography. The running direction of dislocations strongly depended upon the pulling direction; i.e., $[1\ 1\ 0]$, $[\bar{1}\ 1\ 0]$, and $[1\ 1\ 0]$ for crystals grown along the $[112]$ axis and $[010]$ for the crystal grown along the $[010]$ axis. The growth conditions were as follows: (1) pulling rate, 8 mm/hr; (2) crystal rotation rate, 20 rpm; (3) pulling directions $[100]$ $[010]$ and $[112]$; (4) crucible, pyrex glass; and (5) atmosphere, air.

TABLE 1. PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS AND CONDITIONS USED TO GROW CRYSTALS BY THE CZOCHRALSKI METHOD

| Organic Compound | Formula | Molecular Weight | Melting Point (°C) | Pulling Rate mm h ⁻¹ | Crystal Rotation Rate | References |
|-------------------------------|--------------------------|------------------|--------------------|---------------------------------|-----------------------|------------|
| (1) Benzil | $C_6H_5COCO_5H_5$ | 210.23 | 95 - 6 | 0.1 - 0.5 | — | 12 |
| | | | | 0.1 - 0.3 | 8 rpm | 13 |
| (2) Benzophenone | $(C_6H_5)_2CO$ | 182.22 | 48.1 | | — | 12 |
| (3) 12-Tricosanone (Laurone) | $[CH_3(CH_2)_{10}]_2CO$ | 338.63 | 69.3 | | — | 14 |
| (4) Salol (Phenyl salicylate) | $2-(OH)C_6H_4CO_2C_6H_5$ | 214.22 | 43 | | 20 rpm | 15 |

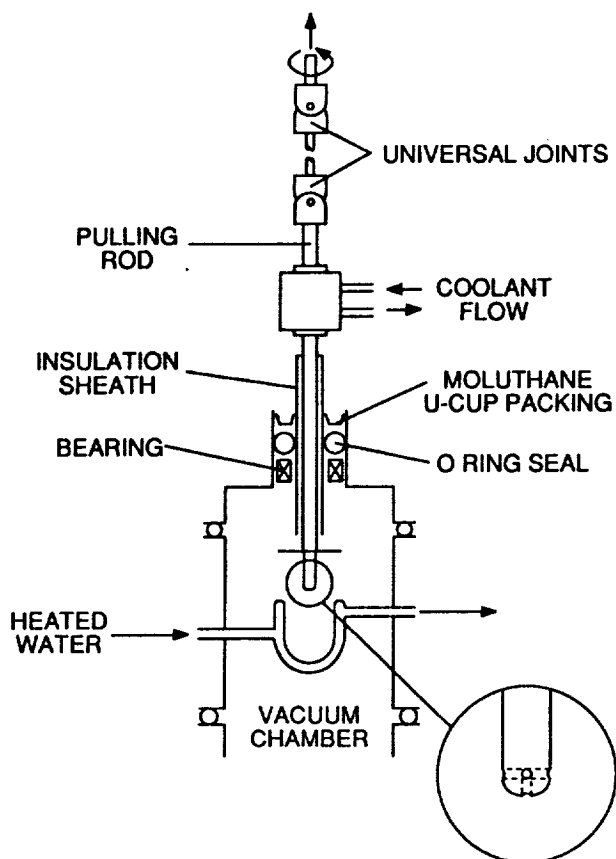


Figure 2. Czochralski apparatus used by Cook and Gwan [14] to grow single crystals of 12-tricosanone (laurone).

III. REVIEW OF PREPARATION METHODS OF THIN SPECIMENS FROM ORGANIC BULK CRYSTALS

Organic crystals are generally mechanically soft since molecular sites are bound only by relatively weak Van der Waals forces; thus, special techniques are needed for the cleavage, cutting, and polishing of organic crystals. This section reviews methods established to prepare thin specimens that are applicable to crystals grown by the Czochralski, Bridgman, vapor, and solution methods.

A. Cleaving

Lipsett [16] cleaved Bridgman grown crystals of naphthalene and anthracene by a method that may be applied to organic crystals grown by other methods. The crystal is removed from the container and examined for clues showing the location of the principle cleavage plane. If it is located, the crystal is easily cleaved by carefully aligning a razor blade with the cleavage plane and applying suitable pressure. If this is not the case, a section about 0.5 in. long is sawed from the end. A razor blade is grasped between the thumb and forefinger of each hand and downward force applied to the top surface of the short length of crystal in various directions in an effort to locate the cleavage plane. If it is not found, the blade may be pressed fairly firmly against the crystal and nothing will happen. If the blade is approximately aligned with the cleavage plane, the crystal will cleave with a fair amount of pressure but the break will be fairly irregular. If the blade is carefully aligned with

the cleavage plane, the crystal will cleave with almost no pressure. A minimum thickness of 1.5 mm was obtained in the cleavage of naphthalene and anthracene single crystals due to crumbling when thinner sections were attempted.

B. Cutting

The most advisable way to cut soft organic crystals is to use a solvent-soaked thread (e.g., a cotton thread) to prepare thin sections by gentle dissolving [10]. Desirable characteristics of the solvent are low vapor pressure and low toxicity. Thin plates of benzil, which is of interest in this laboratory because of its good non-linear optical properties, have been cut using this technique. Bleay et al. [11] used ethanol or ethanol/toluene mixtures to cut 1 to 2 mm thick sections from Czochralski grown boules. Scheffen-Lauenroth et al. [17] used xylene as a solvent to cut 1 to 2 mm thick plates from benzil crystals grown from undercooled melts.

Leininger [18] used mechanical cutting in preparing thin sections of Bridgman grown stilbene crystals. Samples were cut using a hacksaw blade with extreme care; however, any twist in the saw cut resulted in fracture of the crystal. A band saw set up using laboratory equipment was found to be a more refined technique. The blade was a multistranded 0.005-in. stainless steel wire and 400-mesh carborundum was the cutting agent. Gum arabic was added to the abrasive mud to aid in carrying it into the saw cut. The use of a light weight wire as a blade eliminated torsional stresses during cutting of the crystal.

C. Polishing

The polishing of crystals by dissolution using a suitable solvent is preferred to using abrasives in polishing organic crystals. The methods described by Karl [10] is polishing on a solvent-soaked lens tissue on a glass optical flat or the use of a polishing tool equipped with a micrometer screw. Scheffen-Lauenroth et al. [17] polished benzil crystals on a soft cloth wet with xylene. The surface still showed scratches after polishing due to low mechanical strength. These were removed by etching the specimens in xylene for a few seconds.

An example of the abrasive method for polishing crystals is the process used by Leininger [18] to polish Bridgman grown stilbene crystals. After cutting, the rough crystals were surface finished using sand paper. The 200 grit paper was used to remove material and 320 grit paper to yield a finely sanded surface. Next, the surface was polished using 600-mesh carborundum on cheesecloth on a flat surface. All sanding and polishing operations were performed wet. To obtain a very fine polish, moist 600-mesh carborundum was rubbed on the crystal with a finger while wearing gloves.

IV. PROJECTED ADVANTAGES OF CZOCHRALSKI CRYSTAL GROWTH IN MICROGRAVITY

Wenzl [19] examined the feasibility of growing crystals in microgravity by the Czochralski method. The information contained in this section is based on that discussion. Undesirable characteristics of crystal growth by the CZ method on Earth are as follows: (a) the temperature gradient points down, therefore, convection sets in easily and controls heat and mass transfer; and (b) the crystal is subject to

elastic stress because of its own weight, surface tension, and hydrostatic pressure at the interface. The weight of the growing crystal may become larger than the critical stress at which plastic deformation occurs thus deteriorating the quality of the crystal. In microgravity, the hydrostatic pressure is the same everywhere in the melt; therefore, buoyancy driven convection processes are negligible, in contrast to growth on Earth, where they usually dominate the heat and mass transfer. Another benefit of crystal growth in 0-g is the elimination of the deformation of the growing crystal due to its own weight.

Wenzl [19] described two modifications of the Czochralski apparatus that may be used to grow crystals in microgravity. A growth process that does not require a container is shown in Figure 3. The melt tends to form a sphere in 0-g due to the absence of hydrostatic pressure. A nonwetting mask is used to help shape the meniscus at the growth interface. A more advantageous arrangement is shown in Figure 4 which consists of a cylindrical crucible with piston and mask. The crystal growth process may be performed in the following manner: (a) nonwetting melt is contained in cylindrical container; (b) piston induces pressure until the melt protrudes as a hemisphere out of a circular hole in mask; and (c) the seed crystal attached to a pulling rod is brought into contact with the surface of the melt and after equilibration growth is initiated by pulling up the crystal slowly.

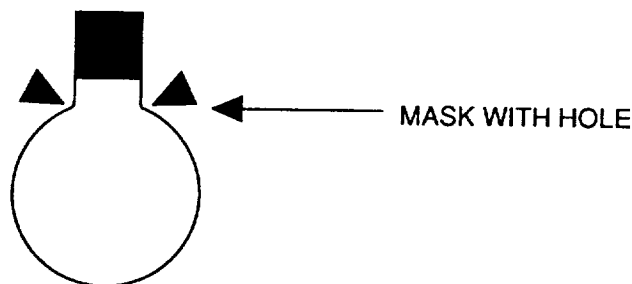


Figure 3. Czochralski growth process in 0-g without crucible that was proposed by Wenzl [19].

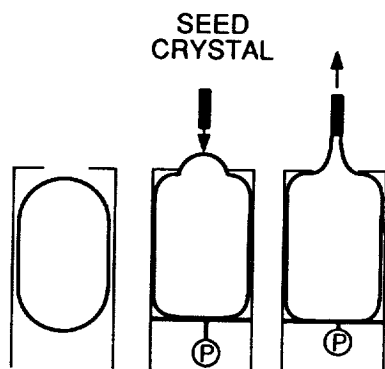


Figure 4. Czochralski growth process in microgravity in a cylindrical crucible with piston that was proposed by Wenzl [19].

Naumann et al. [20] described a Czochralski growth modification that may be used to grow large defect-free organic and inorganic crystals in a spherical container on Earth and in microgravity. Encapsulant in combination with appropriate accessories provide a deformable environment for the growing crystal that allows expansion or contraction without contacting rigid container walls, thus eliminating mechanical strains in the growing crystal. Generally, a seed crystal is attached to a heat conducting rod and positioned inside the spherical interior. The rod extends through the sphere and is connected to a heat sink and an independent temperature controlling device. The melt is heated to some predetermined temperature whereas the temperature of the rod holding the seed crystal is reduced, drawing excess heat through the thermal conducting rod at a controlled rate. The crystal grows to a single, defect-free crystal onto the seed crystal which grows outward in a generally spherical direction. By this method, convection is reduced in a gravity field in the melt, which in turn results in a more perfect crystal. In microgravity, crystalline perfection should be enhanced.

V. CONCLUSION

The literature suggests that the Czochralski method is a promising technique for growth of high quality single crystals of organic compounds. The major advantage of this method, in comparison to growth by the Bridgman and vapor growth methods, is that the CZ method is essentially container free with respect to the growing crystal. This eliminates mechanical damage due to the container wall which hinders the growth of high quality crystals. From the literature, examples were demonstrated by the CZ growth of benzil crystals that had fewer defects than commonly observed in Bridgman grown benzil crystals. The feasibility of using microgravity to grow higher quality crystals than those grown on Earth is promising and will constitute a significant part of this study.

Comprehensive work in this laboratory will examine the effect of processing parameters on the crystal characteristics and nonlinear optical properties of organic materials.

REFERENCES

1. Zyss, J.: J. Molecular Electronics, Vol. 1, 1985, p. 25.
2. Williams, D. J. (Ed.): Nonlinear Optical Properties of Organic and Polymeric Materials. ACS Symposium Series, No. 233, American Chemical Society, Washington, D.C., 1983.
3. Zyss, J.: J. Noncrystalline Solids, Vol. 47, 1982, p. 211.
4. Williams, D. J.: Angew. Chem. Int. Ed. Eng., Vol. 23, 1984, p. 690.
5. Garito, A. F. and Singer, K. D.: Laser Focus, Vol. 80, 1982, p. 59.
6. Garito, A. F., Teng, C. C., Wong, K. Y., and Khamiri, O. Zamani: Mol. Cryst. Liq. Cryst., Vol. 106, 1984, p. 219.
7. Chemla, D. S. and Zyss, J. (Eds.): Nonlinear Optical Properties of Organic Molecules and Crystals, Vols. 1 and 2, Academic Press, New York, 1987.
8. Glass, A. M.: Science, Vol. 226, 1984, p. 657.
9. Ardle, B. J., Sherwood, J. N., and Damask, A. C.: J. Crystal Growth, Vol. 32, 1971, p. 121.
10. Karl, N.: High Purity Organic Molecular Crystals. In Crystals: Growth, Properties, and Applications, H. C. Freyhardt, Managing Editor, Springer-Verlag, New York, 1980, p. 4.
11. Bleay, J., Hooper, R. M., Narang, R. S., and Sherwood, J. N.: J. Crystal Growth, Vol. 43, 1978, p. 589.
12. Jerphagnon, J.: IEEE Journal of Quantum Electronics, 1971, p. 12.
13. Katoh, K. and Kato, N.: J. Crystal Growth, Vol. 73, 1985, p. 203.
14. Cook, J. S. and Gwan, P. B.: J. Crystal Growth, Vol. 33, 1976, p. 369.
15. Inoue, T., Jim, W. Q., and Komatsu, H.: Crystal Res. and Technol., Vol. 20, 1985, p. 195.
16. Lipsett, F. R.: Canadian Journal of Physics, Vol. 35, 1957, p. 284.
17. Scheffen-Lauenroth, Th., Klapper, H., and Becker, R. A.: J. Crystal Growth, Vol. 55, 1981, p. 557.
18. Leininger, R. F.: Rev. Scien. Instrum., Vol. 23(2), 1952, p. 127.
19. Wenzl, H.: Czochralski Growth of Crystals in 0-G and 1-G. In Materials Science in Space with Application to Space Processing, Leon Steg, Ed., American Institute of Aeronautics and Astronautics, New York, 1977, p. 437.
20. Naumann, R. J., Lehoczky, S. L., and Frazier, D. O.: Method and Apparatus for Growing Crystals. U.S. Patent No. 4,738,831, April 19, 1988.

APPROVAL

A PRELIMINARY REVIEW OF ORGANIC MATERIALS SINGLE CRYSTAL
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The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

E. Tandberg-Hanssen

E. TANDBERG-HANSEN
Director, Space Science Laboratory

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| 16. ABSTRACT The growth of single crystals of organic compounds by the Czochralski method has been reviewed. From the literature, single crystals of benzil, a nonlinear optical material with a d_{11} value of $11.2 \pm 1.5 \times d_{11}$ value of α quartz, has fewer dislocations than generally contained in Bridgman crystals. More perfect crystals were grown by repeated Czochralski growth. This consists of etching away the defect-containing portion of a Czochralski grown crystal and using it as a seed for further growth. Other compounds used to grow single crystals are benzophenone, 12-tricosanone (laurone), and salol. The physical properties, growth apparatus, and processing conditions presented in the literature are discussed. Moreover, some of the possible advantages of growing single crystals of organic compounds in microgravity to obtain more perfect crystals than on Earth are reviewed. | | | |
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